Characterization of Low Pressure Cold Plasma in the Cleaning of Contaminated Surfaces

Devin Lanz
John F. Kennedy Space Center
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Devin G. Lanz[*]
University of Dayton, Dayton, OH 45469

Paul E. Hintze[†]
NASA, Kennedy Space Center, FL 32899

The characterization of low pressure cold plasma is a broad topic which would benefit many different applications involving such plasma. The characterization described in this paper focuses on cold plasma used as a medium in cleaning and disinfection applications. Optical Emission Spectroscopy (OES) and Mass Spectrometry (MS) are the two analytical methods used in this paper to characterize the plasma. OES analyzes molecules in the plasma phase by displaying the light emitted by the plasma molecules on a graph of wavelength *vs.* intensity. OES was most useful in identifying species which may interact with other molecules in the plasma, such as atomic oxygen or hydroxide radicals. Extracting useful data from the MS is done by filtering out the peaks generated by expected molecules and looking for peaks caused by foreign ones leaving the plasma chamber. This paper describes the efforts at setting up and testing these methods in order to accurately and effectively characterize the plasma.

Nomenclature

A	= *Amperes*
Ar	= *Argon*
CCD	= *Charge-Coupled Device*
g	= *Grams*
H	= *Hydrogen*
H$_2$O	= *Water*
Hz	= *Hertz*
ID	= *Inner Diameter*
ISS	= *International Space Station*
KF	= *Klein Flange (Quick Flange)*
min	= *Minutes*
mL	= *milliliter*
mm	= *Millimeters*
m/z	= *Mass to Charge Ratio*
MS	= *Mass Spectrometer/Spectrometry*
N	= *Atomic Nitrogen*
N$_2$$^{(+)}$	= *Diatomic Nitrogen (ion)*
NASA	= *National Aeronautics and Space Administration*
O	= *Atomic Oxygen*
O$_2$	= *Diatomic Oxygen*
OD	= *Outer Diameter*
OES	= *Optical Emission Spectroscopy*
·OH	= *Hydroxide Radical*
T	= *Time*
V	= *Volts*
λ	= *Wavelength (nm)*

[*] NIFS Fall Intern, UB-R3, Kennedy Space Center, FL 32899
[†] Senior Scientist, UB-R3, Kennedy Space Center, FL 32899

I.   Introduction

Current cleaning and disinfection methods used in space missions are wasteful. Methods used on the International Space Station, such as disinfecting wipes, result in material waste when the wipes are discarded. To replace these methods, NASA is researching cleaning techniques which result in minimal waste. Low pressure, cold plasma cleaning is one of these methods. By using breathing air as the plasma gas, there are no consumables and no material waste is generated. After the cleaning process, it may be possible for the breathing air plasma to be filtered and reintroduced into the crew's breathing air, leading to minimal resource use.

The goal of this project is to develop a method for characterizing plasma used in decontaminating surfaces in order to understand how effectively it is cleaning the object. Many analytical methods could be used to analyze the plasma, but the two that are in use for this system are optical emission spectroscopy (OES) and mass spectrometry (MS). Analysis and characterization of the plasma will result in a more thorough understanding of the cleaning capabilities of the low pressure cold plasma system. Appropriate applications for the characterizations described in this paper are for plasma used in disinfection of bacterially infected objects, objects contaminated with greases, and any other application using breathing air low pressure cold plasma as a cleaning medium.

II.   Instrumentation and System Setup

An array of instruments and hardware work to generate, observe, and analyze the plasma.   The plasma generator is a self-contained system except for a gas supply, which is a series of K-bottles. The emission spectroscopy system consists of a fiber optic cable, a monochromator, and two detectors, a CCD camera or a photon counter. Only one of the detectors can be used to take measurements during an experiment. The mass spectrometer system takes samples from the plasma through a column or tube attached to the exit port of the chamber.

A. Plasma Generator

The plasma generator used in this experimental setup is from Electronic Diener Plasma-Surface-Technology, model Pico B, fed by a 400V, 5A, 60 Hz power supply. The Diener Pico B includes a touch screen and stylus which is used to edit parameters of an automatic program, such as pump-down pressure and time limit, gas supply time, gas supply ratio, and plasma time and power, and includes start, stop, and emergency stop buttons.

Previous cleaning tests had been conducted using pure oxygen, pure hydrogen, or breathing air as the cleaning medium. After finding that the particular gas used had no significant impact on the effectivity of the cleaning, breathing air was chosen as the medium due to its relative abundance over pure oxygen or hydrogen. The flow of the supply gas is controlled by a mass flow controller onboard the plasma generator, which can handle three gas supplies. The flow rates of gases are controlled automatically by the computer in order to maintain a user-input pressure.

B. Optical Emission Spectroscopy

Plasma is a phase of matter in which molecules are in an excited state, hence its glowing characteristic (figure 1). This glow can be observed using emission spectroscopy. Different species emit photons at a particular wavelength, which is then diffracted by a grating in the monochromator, and the location of the photons with a particular wavelength is measured with a sensor.

The light is transmitted from the chamber to the monochromator through a fiber optic cable aimed into the plasma. This cable transmits light to a slit in the side of the monochromator, which then uses a mirrors to reflect the light off of a grating and out of an exit slit (figure 2). The grating separates the light into its separate wavelengths, giving each wavelength a different physical location. This difference in location can then be measured using a CCD Camera, or a photon
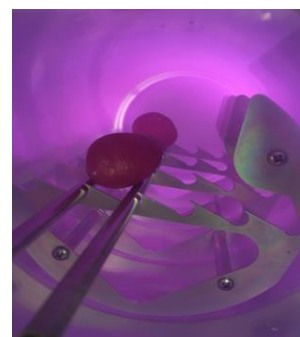
Figure 1. Radishes in Plasma
This is an image of inside the plasma chamber. Pictured are radishes inoculated with the bacteria B. pumilus.
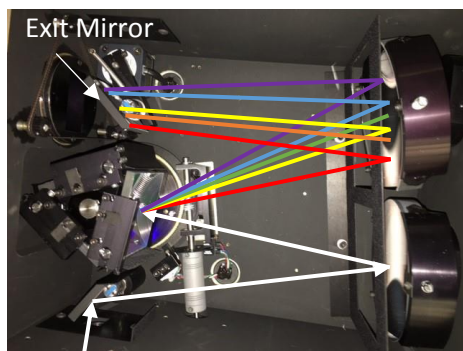
Figure 2. Monochromator Schematic *Light enters from the slit on the left, reflects of Mirror M3 and M1, is refracted by the grating into its constituent wavelengths, and then exits either out the side or rear slits.*

counter, which would be attached to one of the two exit slits on the monochromator. The exit mirror rotates to reflect the light out of the side or back exit slit.

The monochomator used in this particular set up is an Acton SP2300 by Princeton Instruments. The CCD camera used is a PIXIS 100 by Princeton Instruments, used to detect the location of different wavelengths and measures their intensities. This camera is attached to the rear exit slit, while a PD-473-1 Photon Counting Detector, also from Princeton Instruments, is attached to the side exit slit. The CCD camera is able to detect a larger range of wavelengths over a given time period as compared to the photon counter, though only detects those above about 315 nm. The photon counter is useful for detecting wavelengths down to about 190 nm, though is it a much slow process than the CCD camera. 190 nm is the low limit because below that, oxygen begins to absorb light, preventing detection.

The software used to record data are WinSpec 32 initially, and then Lightfield V4.0 for the CCD camera, and SpectraSense V4.02 for the photon counter. WinSpec 32 did not have the capability to identify peaks or export a spectrum as an image, but was able to export data to a CSV file in ASCII format, and a program was written in Excel VBA to take this data, create a graph, and estimate peaks. However, the new program, Lightfield, has the capability to identify peaks and export spectra as an image. SpectraSense also has the capability to export spectra as an image.
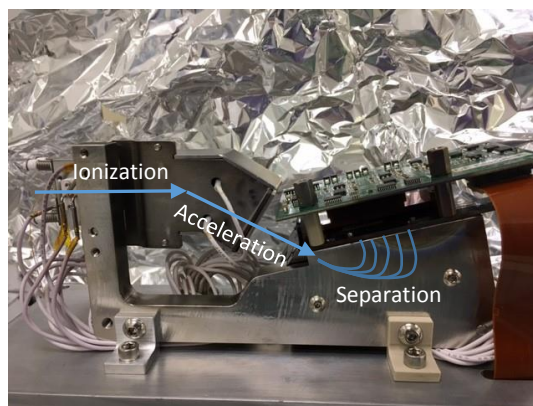
C. Mass Spectrometry

The mass spectrometer used in this experimental set up is an IonCam 2020. This model was designed to house a micro gas chromatograph and a roughing pump as well as the MS, however these two elements had been removed. While the gas chromatograph is not necessary, an external oil pump needed to be used as the roughing pump for the turbomolecular pump. The IonCam 2020 has an onboard computer and operating system, and a touchscreen display on the front panel, requiring minimal external hardware to operate. The MS is attached to the plasma chamber though a KF T-connection in the plasma vacuum line (figure 3).

Mass spectrometry uses the mass to charge ratio of a molecule to separate it from other molecules. Gas is fed into the MS ionization region, which is located in ultra-high vacuum. The ionizer bombards the gas with a stream of electrons which will strip away electrons from the gas molecules resulting in ions, both the original mass of the molecule as well as fragments of it. The amount of one fragment compared to others depends on its relative stability. These ions are then repelled toward a magnet which curves the path of the ions, causing them to travel over a CCD camera and contact the camera at different locations based on the mass to charge ratio of the ion (figure 4).

Figure 3. Mass Spectrometer Connection *The plasma chamber is evacuated using a solenoid valve (right), through a hose to an oil pump (right). The MS is connected though the T-connector in the vacuum line.*

Figure 4. Ion Path in a Mass Spectrometer *Molecules are inserted into an ionization chamber, ionized, accelerated, deflected by a magnet, and detected by a sensor.*

Mass Spectrometry will be used to detect foreign molecules which are removed by the plasma and carried out of the chamber. Greases or biological proteins would have different masses than nitrogen and oxygen found in air, and therefore should be easily detectable using the MS.

III.   Results and Discussion

The goal of these experiments was to develop a method to characterize the plasma in order to more fully understand its composition as it exits the chamber. Optical Emission Spectroscopy and Mass Spectrometry were used in analyzing the plasma. OES is able to analyze the plasma in its excited state by recording the wavelengths of photons emitted by the plasma molecules, while MS can detect molecules that do not emit light or are otherwise undetectable by OES. Through the course of experimentation, several different configurations for both MS and OES were used, all of which will be discussed below.

B. Optical Emission Spectroscopy

Characteristic peaks of particular molecules for reference were gathered in two different ways. The first was through research of literature which reported wavelengths of particular molecules. The second way characteristic wavelengths were found was using energy values taken from the NIST chemistry database. This collection of wavelengths was assembled into a database on a spreadsheet, and a program was written using Excel VBA which locates peaks in a data set, and identifies to what molecules the peaks correspond. Later on, when Lightfield was used, the newer of the two spectroscopy programs, it was able to identify peaks on its own, at which point all that had to be done was match molecules with the labeled peaks.

1. Initial Experimental Setup

The first experimental setup used to capture emission spectra consisted of the CCD camera, the monochomator, and the fiber optic cable. The fiber optic cable was attached to a stand which was placed in front of the viewing port on the plasma chamber (figure 5). The monochromator was set up to take a spectrum from $\lambda = 350$ to $\lambda = 950$. This setup was used at first because it was simple to set up and remove. However, it had the disadvantage that the glass viewport absorbs light in the ultraviolet region, and the glass reflects ambient room light into the fiber optic cable.

Emission spectra taken from this set up show peaks characteristic of Mercury, Europium, Yttrium, and Terbium, none of which should be in the plasma, but are in fact found inside standard fluorescent lightbulbs[2]. This confirms that light from bulbs in the lab reflected off the glass door, providing a substantial signal in spectra, even with all lights (except the emergency lights) turned off. Experiments with this setup were aimed at characterizing the plasma with no foreign species in the chamber; detection of such trace amounts of contaminants required greater clarity.

2. Additional Setups

The fiber optic cable was attached to the back of the chamber via a KF fitting allowed the fiber optic cable to directly measure light in the plasma chamber. The adapter provided a vacuum-tight seal, and minimized the amount of room lights seen by the cable (figure 6). However, coming in from the back of the chamber, the fiber optic cable faced directly at the view port, meaning room light would come in through the view port, so the emission spectra still reflected peaks characteristic of fluorescent lights. A layer of aluminum foil placed over the viewport, was able to effectively seal off all points through which room light might leak into the chamber.
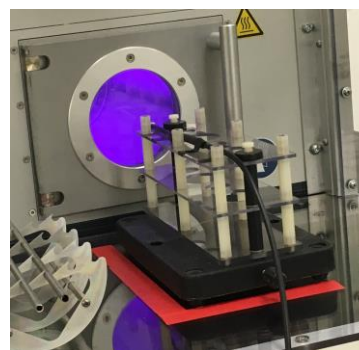
Figure 5.   Initial OES Setup *The fiber optic cable was aimed into the plasma through the quartz class viewing port. The other end of the cable leads into the side entrance slit on the monochomator*
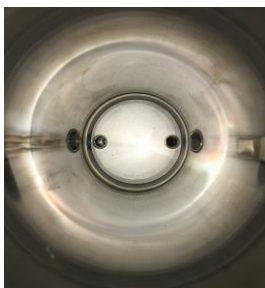
Figure 6. Plasma Chamber
Inside the cylindrical plasma chamber with the fiber optic cable port on the left of the back plate, and the pressure transducer on the right.

With the new set up, tests could now be conducted in an attempt to identify trace amounts of contaminant. Two experiments were conducted in order to perform this characterization. The first was using an arbitrary mass of steel wool contaminated with 1mL of "Witch's Brew," a mixture of fluorinated greases containing equal parts Krytox® 240AC, Braycote 601EF, MIL-PRF-5606, MIL-PRF-83282 (aircraft lubricants), and dioctyl sebacate in Vertrel™ MCA, at a concentration of 1.124g of each constituent (5.620g total) per 100 mL solution. The steel wool rusted too easily, which made weighing the wool before and after treatment an invalid method of analysis. Thus, the second experiment conducted was the same test using copper wool, which would be much less resistant to oxidation. In both experiments, the wools were contaminated, and exposed to plasma treatment for T = 5 min, T = 10 min, and T = 15 min, as well as 15 minutes under vacuum with no plasma as a control. Emission spectra were taken every 2.5 minutes using the CCD Camera and a "Step and Glue" process.

For later testing, the photon counter was attach to the side exit slit of the monochomator. Tests done with this configuration were focused on looking for the presence of hydroxide radicals (·OH) which is a very reactive molecule and could be interacting with other species in the plasma. Peaks generated by ·OH are found in the range λ = 306 to 309[3] (see table 1).

3. Results

Emission Spectrscopy has proven to be a viable method in characterizing plasma. Breathing air plasma is easily identified by a wide array of peaks ranging from the ultraviolet region to infrared, specifcally the values of λ=300 to λ=950 (figure 7 & table 1). However, OES is only able to identify contaminants in a plasma if the contaminant contributes to the emission of the plasma.

| Species	Identified Peaks (nm)
N$_2$	315.8, 337.0, 353.5, 357.5, 375.4, 380.3, 399.6 [3]
N$_2^+$	391.3[3], 427.7, 470.8, 522.6 [1]
Other N$_2$ and Derivatives	570-775, 799.3, 850-891 (except peak at 656.1)
H	656.1, 486.0 [3]
O	777.4, 844.5, 926.5
·OH	306.8[4], 308.0[5], 309.0[6]
Unidentified Species (in both air and water)	500.0, 560, 567.8, 780, 782.7, 855.5, 862.7, 867.8
Present only in Greased Wool	519.5

Table 1. Identified Peaks and their Corresponding Species in an Emission Spectrum *Peaks measured were compared to those researched and calculated using known energy levels at certain states.[1, 3-6]*
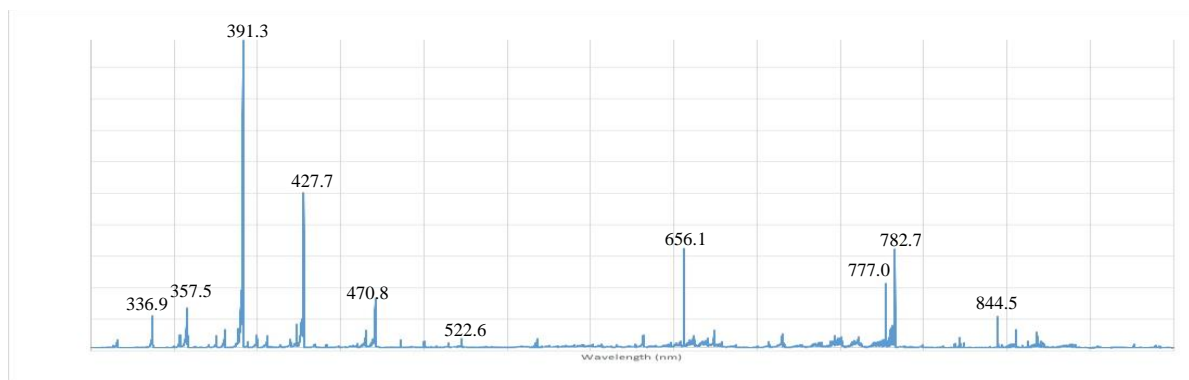
Figure 7.   Emission Spectrum of Air Plasma at 0.4 mbar with Peak Labels
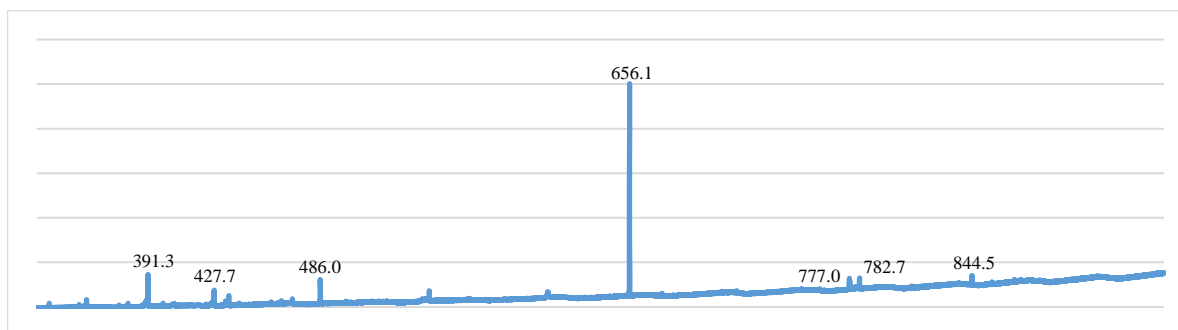
Figure 8.   Radish in Plasma Treatment at 0.8 mbar, T = 15 minutes
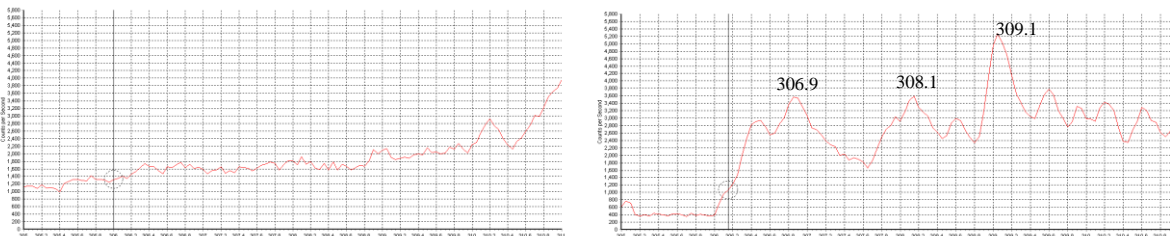
Figures 9 & 10.   Emission Spectra from λ = 305 to λ = 311 using Photon Counter *Figure 9 (left) shows a spectrum taken with an empty chamber of dry air plasma. Figure 10 (right) shows a spectrum taken with dry air plasma, but with a water-saturated wipe in the chamber. The peaks corresponding to ·OH are labeled in graph 6, though offset by +0.1 nm compared to values in table 1 due to instrument calibration differences.*
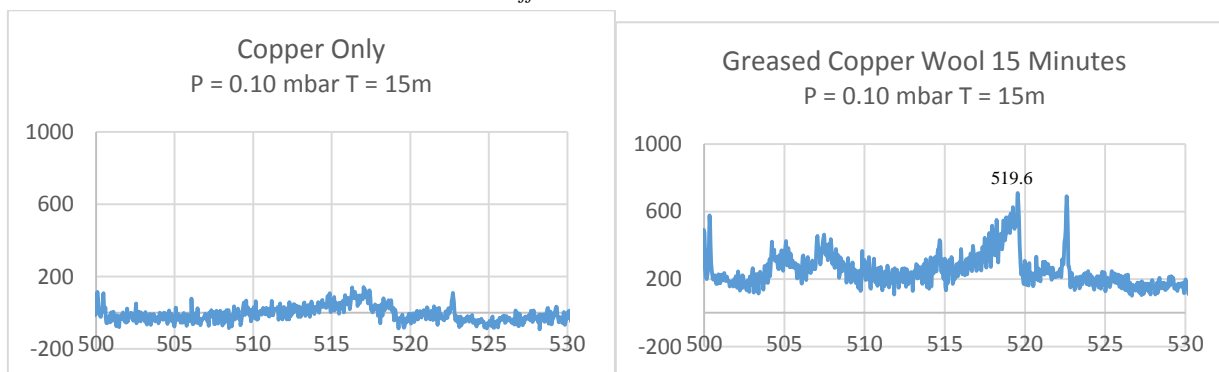
Figures 11 & 12.   Examples of Emission Spectra using CCD Camera. *Figure 11 (left) is an excerpt (λ = 500 to 530) of a spectrum taken while copper wool was being exposed to plasma at T = 15. Figure 12 (right) is an excerpt of the same range of a spectra at the same time, except the copper was wool contaminated with fluorinated greases was undergoing plasma treatment. There is an obvious peak at λ = 519.6 in figure 12 that is not present in figure 11.*

Other than identifying the peaks for air, OES was useful in indicating the presence of water, by identifying the peak for atomic hydrogen, which could only have been split off from a water molecule. When produce underwent plasma treatment, there was a significant presence of water as compared to an empty plasma chamber (figure 7 vs. figure 8). This discovery explained why some produce which underwent treatment suffered severe damage due to dehydration.

Using the photon counter, the presence of ·OH was also detected (figures 9 & 10). ·OH is an extremely reactive intermediate species, also split off from a water molecule, and it may explain presence of abnormal molecules in the plasma. For example, when large amounts of hydrocarbons are subjected to plasma treatment, radical polymerization occurs, using ·OH as the initiating species. OES was also able to identify a peak related to the the removal of a grease contaminant from copper wool (figures 11 & 12). This information can be used to confirm the presence of a grease contaminanation, or to track the process of its removal.
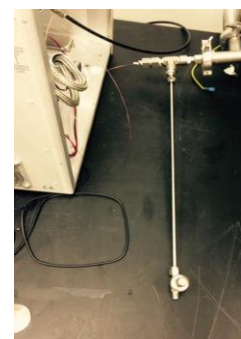
## C. Mass Spectrometry

1. Set-up and Sampling

The MS had to be set up so that it could sample the gas exiting the plasma chamber, which had a pressure between 0.1 and 1 mbar. Difficultly came about in setting up the MS to accept samples because the pressure on the sample side was lower than would normally be used with this specific instrument, which is designed to be injected with a sample at atmospheric pressure. As such, the IonCam 2020 instrument came equipped with a capillary column with an ID of 0.32 mm and OD of 0.40 mm. A longer column allows the MS to handle higher pressures without breaking vacuum, at the expense of a lower sample flow rate into the MS. Therefore, as the plasma chamber operates at 1 mbar or lower, the sample flow rate was too low.

The length of the capillary was shortened by some amount, usually between 1/3 and 1/2 of the previous length, and tested again in an attempt to increase sample flow rate. This process was repeated until the column was as short as it could be, about 12" from the MS to the plasma chamber vacuum line. With still no signal present, a capillary column with a larger ID of 0.32mm and OD of 0.54mm was installed into the MS. This column was not only fused silica, but had a metal coating as well, and the metal could have been interfering with the electronics in the MS, though no tests were done to definitively prove this.

Figure 13. Vent Valve
The needle valve (bottom) was attached to the vacuum line via a Swagelok ® T-Union.

After shortening the capillary to minimal length, it was determined that the feed pressure was still too low to transmit sample though the capillary column. A needle valve was added in order to vent the line and increase the sample feed pressure in an effort to see a signal (figure 13). The vacuum line pressure was too low to see signal when
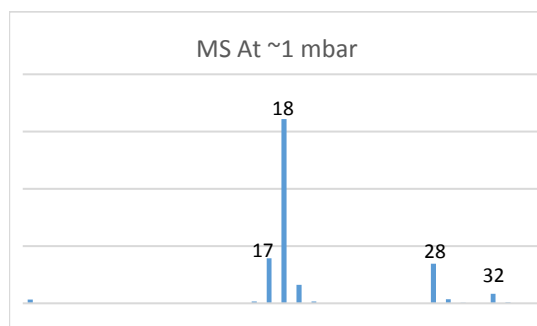

Figure 14. Mass Spectrum Taken at ~ 1 mbar
During venting of a plasma run (with no contaminants), using the final configuration, this spectrum was taken, which clearly shows a major peak at 18 m/z, corresponding to the molecular ion of water, H_2O^+. Water has typically been abundant in all vacuum tests, most likely originating from water molecules absorbed into the walls of the chambers.
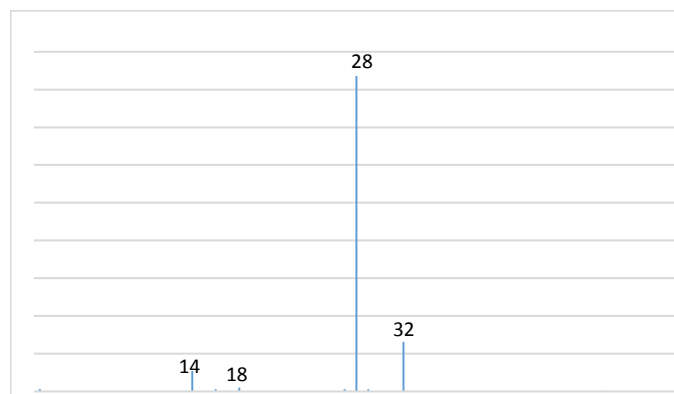
Figure 15. Mass Spectrum of Air taken at Atmospheric Pressure
Peaks for air are located at 14 (N), 18 (H_2O), 28 (N_2), 32 (O_2), and, though not visible on this scale, 16 (O), and 40 (Ar)
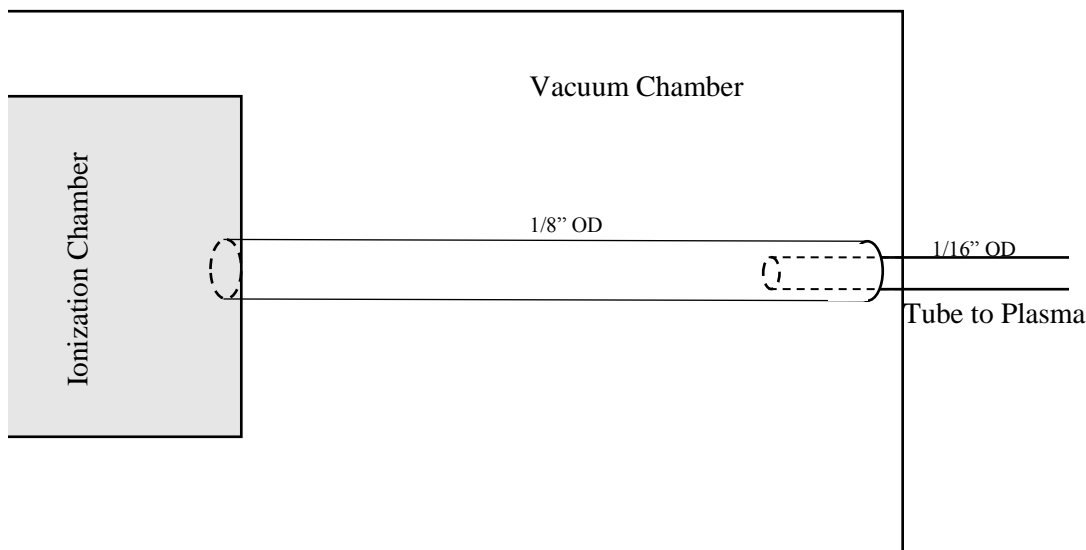
Figure 16. **Diagram of Tubing into MS** *1/16" OD tube (far right) passes into the vacuum chamber through a compression fitting, and is then loosely fit into a larger 1/8" OD tube, which is then slipped over fitting that leads into the ionization chamber.*

the vent was closed, but too high when at atmospheric pressure. Even opening the needle valve completely during vacuum operation did not increase the feed pressure by a significant amount. When the vacuum was off, and the line was vented from vacuum up to about 15 to 20 mbar, the MS began picking up a signal, however, any higher and the MS chamber would exceed nominal pressure; a larger ID tube was still needed to increase the flow rate of sample.

To remedy this problem, as well as use tubing without metal to interfere with electronics and magnets, a larger polyethylene tubing with 1/16" OD was used from the T-connecter in the vacuum line through the port entering the MS vacuum chamber, then a larger 1/8" OD and 1/16" ID silicone tubing was used from inside the vacuum chamber port to the ionization chamber (Figure 16). By using the larger tubes, a sufficient amount of sample was able to be passed from the plasma chamber to the MS, especially during pump-down and venting, since those are the times when the contents of the plasma chamber are constantly being pulled though the vacuum lines. The final configuration remains as it was initially set up (refer to figure 4), with the exception of the use of larger tubes instead of capillary columns.

2. Results

Mass Spectrometry will be useful in detecting molecules which are non-luminescent, or otherwise undetectable by OES. Air generates a consistent mass spectrum when the instrument samples air at atmospheric pressure. When sampling the plasma chamber which is under vacuum, the spectrum changes and water is the dominant species (figure 14). It is most likely that the water that causes this peak comes from trace amounts of water that had been absorbed to the walls inside the MS chamber, and it is the larger peak because very little air makes it through the capillary sample tube.

Unfortunately, tests have not yet been done using MS to characterize plasma. One would expect to see the usual constitents of breathing air, though in what ratios in unknown. In addition, the MS would detect molecules formed from breathing air constituents, such as those derived from reactions with ·OH, or any of the other electronically excited molecules in the plasma.

V. Conclusion

The two analytical methods described in this paper are both suitable for characterizing the breathing air plasma used as a cleaning medium for contaminated surfaces. The analysis of emission spectra has identified major components of air plasma and their peaks in the spectra. Knowing these peaks will make it possible to identify new peaks against a basline spectra, indicating a foreign species in the plasma. MS will help to positively settle any discrepancies in OES data (if any), detect molecules which may not have produced an emission, and detect those that

may not have formed in the plasma, but formed after the plasma reverted to the gas phase. Plasma characterizations, could be used to monitor the progression of a process, detect low levels of contaminants on a surfaces, or identify a plasma or consituents thereof given properties of the plasma.

Though instrument configurations may change as necessary to obtain better measurements, future tests will include data collection using the MS to identify foreign molecules in the plasma as it exits the chamber. Tests with OES will be continued to identify more peaks in emission spectra which correspond to contaminants or abnormal molecules, such as polymers, or derivations of nitrogen and oxygen. If this plasma characterization is succesful, other cold plasma experiments will be able use such data to efficiently characterize their plasma and better understand how the plasma interacts with its environment.

Acknowledgments

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